

AD-A037 967

COLUMBIA UNIV NEW YORK DEPT OF CHEMISTRY
STATE IDENTIFICATION OF REACTION PRODUCTS.(U)
MAR 77 R N ZARE

F/G 20/5

UNCLASSIFIED

AFOSR-TR-77-0215

AF-AFOSR-2551-73
NL

| OF |
AD
A037967



END

DATE
FILMED
4-77

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

READ 4 4 4 4 4 4

AD A 037967

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|--|-----------------------|--|
| 1. REPORT NUMBER AFOSR - TR - 77 - 0215 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) STATE IDENTIFICATION OF REACTION PRODUCTS | | 5. TYPE OF REPORT & PERIOD COVERED Final Scientific 6/1/73 to 2/28/77 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s) Richard N. Zare | | 8. CONTRACT OR GRANT NUMBER(s) AFOSR-2551-73 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemistry Dept., Columbia University New York, NY 10027 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2303/B1, 61102F |
| 11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Directorate of Chemical Sciences /NC Bolling AFB, Washington, DC 20332 | | 12. REPORT DATE Mar 1977 |
| | | 13. NUMBER OF PAGES nine (9) |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Final rept. 1 Jun 73 - 28 Feb 77 | | 15. SECURITY CLASS. (of this report) Unclassified |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) D D C RECEIVED APR 8 1977 REGISTRY | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) chemical laser; chemiluminescence; molecular beam; laser-induced fluorescence | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The final scientific report contains a chronological bibliography of 14 publications supported by this contract, as well as a brief summary emphasizing our attempts to make a prototype chemically-driven electronic transition laser. | | |

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

402 330

C FILE COPY

MAR 11 1977

FINAL SCIENTIFIC REPORTApproved for public release;
distribution unlimited.

Period: June 1, 1973-February 28, 1977

Contract: AFOSR-73-2551

Title: The State Identification of Reaction Products

Institution: The Trustees of Columbia University
in the City of New York

Principal Investigator: Richard N. Zare
Richard N. Zare
Higgins Professor of Natural Science
Department of Chemistry
Columbia University
New York, NY 10027
(212) 280-2017

Acknowledgment: Research sponsored by Air Force Office
of Scientific Research, AFSC, USAF

Distribution: Approved for public release;
distribution unlimited

| | |
|---------------------------------|-------------------------------------|
| Public Section | <input checked="" type="checkbox"/> |
| Restricted Section | <input type="checkbox"/> |
| Unrestricted Section | <input type="checkbox"/> |
| DISTRIBUTION/AVAILABILITY CODES | |
| REF. | AVAIL. and/or SPECIAL |
| A | |

D D C
RECEIVED
APR 8 1977
RECEIVED
D

AD 00

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DDC
This technical report has been reviewed and is
approved for public release IAW AFR 190-12 (7b).
Distribution is unlimited.
A. D. BLOSE
Technical Information Officer

Availability Statement:

Qualified requester may obtain additional copies from the Defense Documentation Center; all others should apply to the National Technical Information Service

Condition of Reproduction:

Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

A. Chronological Bibliography of Publications Supported
By AFOSR-73-2551

- 1.* P. J. Dagdigian, H. W. Cruse and R. N. Zare, "Radiative Lifetimes of the Alkaline Earth Monohalides," J. Chem. Phys. 60, 2330 (1974).
- 2.* R. N. Zare and P. J. Dagdigian, "Tunable Laser Fluorescence Method for Product State Analysis," Science 185, 739 (1974).
- 3.* P. J. Dagdigian and R. N. Zare, "Primitive Angular Distribution Studies of Internal States in Crossed-Beam Reactions Using Laser Fluorescence Detection," J. Chem. Phys. 61, 2464 (1974).
- 4.* P. J. Dagdigian, H. W. Cruse, A. Schultz and R. N. Zare, "Product State Analysis of BaO from the Reactions Ba + CO₂ and Ba + O₂," J. Chem. Phys. 61, 4450 (1974).
- 5.* H. U. Lee and R. N. Zare, "Flame Emission Studies of Ozone with Metal Alkyls: Zn(CH₃)₂ and Zn(C₂H₅)₂," Combustion and Flame 24, 27 (1975).
- 6.* P. J. Dagdigian, H. W. Cruse and R. N. Zare, "Laser Fluorescence Study of AlO Formed in the Reaction Al + O₂: Product State Distribution, Dissociation Energy, and Radiative Lifetime," J. Chem. Phys. 62, 1824 (1975).
- 7.* J. G. Pruett and R. N. Zare, "Lifetime-Separated Spectroscopy: Observation and Rotational Analysis of the BaO A' ¹Π State," J. Chem. Phys. 62, 2050 (1975).
- 8.* R. C. Oldenberg, C. R. Dickson and R. N. Zare, "A New Electronic Band System of PbO," J. Mol. Spectrosc. 58, 283 (1975).
- 9.[†] C. R. Dickson, H. U. Lee, R. C. Oldenberg, and R. N. Zare, "Efforts to Develop a Prototype Electronic-Transition Laser From the Chemical Reactions of Laser-Generated Metal Vapors," Proceedings of the Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Massachusetts, Sept. 17-19, 1975 (M.I.T. Press).

- 10.* J. G. Pruett and R. N. Zare, "State-to-State Reaction Rates: Ba + HF(v=0,1) → BaF(v=0-12) + H," J. Chem. Phys. 62, 2050 (1975).
- 11.*† R. N. Zare, "Laser Fluorimetry," Lecture Notes in Physics, Vol. 43, (Springer-Verlag, New York, 1975) p. 112.
- 12.* F. Engelke, R. K. Sander, and R. N. Zare, "Crossed-Beam Chemiluminescent Studies of Alkaline Earth Atoms with ClO₂," J. Chem. Phys. 65, 1146 (1976).
- 13.** F. Engelke, J. C. Whitehead, and R. N. Zare, "The Four-Centre Reaction of I₂^{*} + F₂ Studied by Laser-Induced Chemiluminescence in Molecular Beams," General Discussion No. 62 on "Potential Energy Surfaces," Faraday Society, 1976 (in press).
- 14.** F. Engelke and R. N. Zare, "Crossed-Beam Chemiluminescence: The Alkaline Earth Rearrangement Reaction M + S₂Cl₂ → S₂^{*} + MCl₂," Chemical Physics.(in press).

* Reprints received by AFOSR.

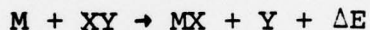
† Preprint enclosed; no reprints available.

*†Preprint received by AFOSR; no reprints available.

**Preprints received by AFOSR; reprints will be forwarded on publication of article.

B. Summary

As stated in the introduction to the original proposal, the use of chemical energy to drive a laser system is attractive from both the standpoints of efficiency of operation and energy storage capabilities. Many research groups have been and continue to be engaged in the search for such a chemical laser. Unfortunately, no one has yet succeeded. Although there are many metal-oxidant reactions



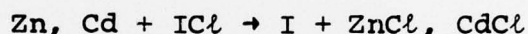
that are highly exothermic, and thus candidates for laser driving systems, two obstacles must be overcome to produce a chemical laser: the metal has to be produced in the vapor phase at high densities; and the energy liberated from the reaction must be channeled to produce a population inversion in the lasing species.

The first problem was attacked here through the use of a laser blow-off technique^{1,2} to provide the required high metal atom fluxes. With this method, the reactions of Cu, Al, Ba, and Sn with the oxidizers N₂O and F₂ were studied. In many instances, bright chemiluminescence was observed with an optical

multichannel analyzer, but all attempts to find laser emission were futile. It has since been found³ that the metal vapor produced by laser blow-off rapidly condenses to form minute suspended particles under conditions similar to those used in the above studies. Such particles destroy the Q of the laser cavity and would have prevented lasing even if a population inversion had been produced by the reactions. It is possible that there are conditions under which the formation of particles can be eliminated, but this problem severely limits the utility of this technique as a general diagnostic tool.

All of the reactions studied are sufficiently exoergic to produce the MX in an excited electronic state. However, studies of the various reactions under beam conditions show⁴ that, while some excited state products are formed, the bulk of the MX is found in the ground electronic state with much of the excess energy appearing as vibrational and rotational excitation. The energy that is deposited in the excited electronic states is also spread over many vibrational and rotational levels. Both of these problems may be overcome by transferring the energy stored in the MX, both vibrational and electronic, to an atomic system. Preliminary work has

been done on such a scheme using rare-earth metals, primarily Sm, as both the metal reactant to produce the energy and the atomic acceptors of the energy. Such a system holds promise since the rare-earths have low lying electronic states that can be populated by energy transfer and laser emission has been observed from these states.⁵ In an attempt to directly produce excited atoms, the reactions



have been studied. Angular momentum propensity rules indicate that the I atoms liberated should be predominately in the excited $^2P_{1/2}$ state leading to the possibility of laser emission at 1.315μ . A conventional photodissociation I^* laser has been built to probe these reactions systems for the presence of $\text{I}(^2P_{1/2})$.

Since ground state reactants lead primarily to ground state products, work is currently under way to investigate the reactions of excited state species to see if the production of excited state products can be enhanced. One potential laser system has been investigated. A doubled, high power Nd^{3+} : YAG laser was used to excite I_2 to the B state which was then

reacted with F_2 . Although laser emission from the I_2 as well as chemiluminescence from the IF was observed, no laser transitions in IF were found.

Although no chemically-driven laser emission has been found, several problems have been delineated and the direction of future effort indicated. A way must still be found to produce large metal atom concentrations. Certain possibilities, besides the attempt to eliminate particle formation in laser blow-off generation, include the use of exploding wires and the dissociation of organometallic compounds. Effort must also be expended in the study of energy transfer from high vibrational levels of metal diatomics to metal atoms. The search for schemes of direct production of excited atoms by chemical reaction should also continue. And finally, there should be further investigation of the reactions of excited species.

The above has been written as a summary of our attempts to make a prototype chemical laser. However, during this grant period significant progress has been made on developing basic techniques for understanding reaction kinetics on a microscopic level. This is attested to by the papers published during this period.

References

- ¹J. F. Friichtenicht, Rev. Sci. Inst. 45, 51 (1974).
- ²C. R. Dickson, H. U. Lee, R. C. Oldenberg, and R. N. Zare, "Electronic Transition Lasers", J. I. Steinfeld, ed., M.I.T. Press, 1976, p.43.
- ³R. C. Oldenberg, private communication.
- ⁴C. R. Dickson, S. M. George, and R. N. Zare, "Determination of Absolute Photon Yields Under Single-Collision Conditions", J. Chem. Phys. (in press).
- ⁵P. Cahuzac, Le J. De Physique, 32, 499 (1971).